

# Investigation of the Transformation of Uranium under Iron-Reducing Conditions: Reduction of U<sup>VI</sup> by Biogenic Fe<sup>II</sup>/Fe<sup>III</sup> Hydroxide (Green Rust)

Edward O'Loughlin<sup>1</sup>, Michelle Scherer<sup>2</sup>, Kenneth Kemner<sup>1</sup>, and Shelly Kelly<sup>1</sup>

<sup>1</sup> Environmental Research Division, Argonne National Laboratory and <sup>2</sup> Department of Civil and Environmental Engineering, University of Iowa

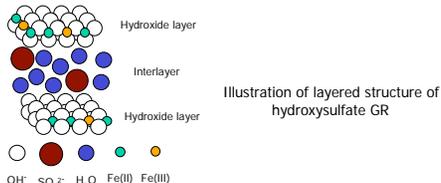
## Background

Many activities associated with the mining, extraction, and processing of U for nuclear fuel and weapons have generated substantial quantities of waste materials contaminated with U and other radionuclides. In many cases, past practices relating to the handling and storage of such waste materials have resulted in extensive contamination of the subsurface. For radionuclides such as U and Tc, species that are stable in oxic environments (e.g., U<sup>VI</sup> and Tc<sup>VII</sup>) are generally thought to be more soluble/mobile than more reduced species (e.g., U<sup>IV</sup> and Tc<sup>IV</sup>). Thus the transformation of radionuclides like U and Tc (as well as metals like Cr) from an oxidized/potentially mobile form to a more reduced/potentially less mobile form is viewed as an attractive approach for their immobilization/stabilization in situ.

Although many microorganisms may directly reduce U<sup>VI</sup> to U<sup>IV</sup>, U<sup>VI</sup> may also be reduced by reductants directly or indirectly formed by the metabolic processes of facultative and strict anaerobes, particularly dissimilatory iron(III)-reducing bacteria (DIRB) and sulfate-reducing bacteria. The reduction of Fe<sup>III</sup> by DIRB typically results in the production of a suite of Fe<sup>II</sup> species, including soluble Fe<sup>II</sup> complexes; Fe<sup>II</sup> surface complexes with organic and inorganic solid phases; and a host of Fe<sup>II</sup>-bearing minerals including magnetite, green rust (GR), siderite, and vivianite.

The reduction of U<sup>VI</sup> to U<sup>IV</sup> by many Fe<sup>II</sup> species is thermodynamically favorable. However, studies of U<sup>VI</sup> reduction by Fe<sup>II</sup> species to date have focused primarily on Fe<sup>II</sup> sorbed to Fe<sup>III</sup> oxyhydroxides. Recently we reported the reduction of U<sup>VI</sup> to U<sup>IV</sup> by hydroxysulfate GR resulting in the formation of nanoparticulate uraninite (*ES&T* 37:721-727, 2003).

Green rusts are mixed Fe<sup>II</sup>/Fe<sup>III</sup> hydroxides which have layered structures consisting of alternating positively charged hydroxide layers and hydrated anion layers.



Green rusts typically form under weakly acidic to alkaline conditions in suboxic environments and have been identified as products of both abiotic and microbially induced corrosion of iron and steel. Indeed, the formation of GRs in zero-valent iron permeable reactive barriers is commonly observed. In addition, GRs are metastable intermediates in the transformation of Fe<sup>II</sup> to magnetite and Fe<sup>III</sup> oxyhydroxides (e.g., lepidocrocite and goethite) under near neutral to alkaline conditions and are believed to play a central role in the redox cycling of Fe in many aquatic and terrestrial environments.

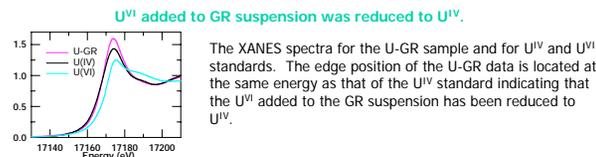
The biogenic formation of GRs was first reported in studies of the microbially mediated reduction of iron and steel; however, the formation of GRs by bacteria known to be key players in the biogeochemical cycling of Fe in aquatic and terrestrial environments has recently been reported. Green rusts have been observed as products of Fe<sup>III</sup> oxyhydroxide reduction by DIRB as well as the anaerobic biooxidation of Fe<sup>II</sup>.

Green rusts have been shown to be capable of reducing a number of organic and inorganic contaminants including nitrate and nitrite, selenate, chromate, and a number of halogenated hydrocarbons.

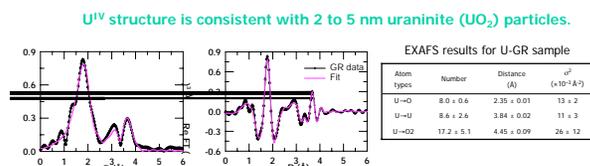
A recent study of the reduction of U<sup>VI</sup> in aqueous suspensions of goethite by the DIRB *Shewanella putrefaciens* strain CN32 by Fredrickson et al. (*GCA* 64:3085-3098, 2000) indicates that the reduction of U<sup>VI</sup> in Fe<sup>III</sup> reducing environments may result from coupled biotic and abiotic processes. In this study we propose to examine the reduction of U<sup>VI</sup> by biogenic green rusts (specifically, green rusts resulting from the reduction of Fe<sup>III</sup> oxyhydroxides by DIRB) and the implications of this process for coupled biotic-abiotic U<sup>VI</sup> reduction in Fe<sup>III</sup>-reducing environments.

## Reduction of U<sup>VI</sup> by Green Rust

### U-GR XANES Results



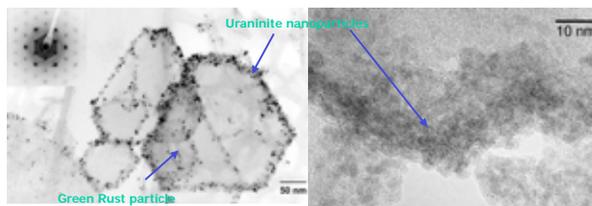
### U-GR EXAFS Results



The Fourier transform of the U-GR EXAFS data and the best-fit theoretical model based on the structure of uraninite (UO<sub>2</sub>). The coordination number of U atoms is less than in bulk uraninite (12), indicating a small particle with comparable numbers of interior and surface U atoms. 8.6 U neighbors is consistent with a particle size of 2-5 nm.

### U-GR TEM Images and Micro-XRD

TEM images and micro-X-ray diffraction measurements confirm formation of uraninite nanoparticles on the surface of the hexagonal GR particles.



**LEFT** - Dark field TEM image (contrast inverted for ease of printing) made using arcs of the (111) and (200) diffuse rings of the electron diffraction pattern of UO<sub>2</sub> clearly showing formation of discrete particles of UO<sub>2</sub> primarily along the edges of the hexagonal GR crystals. The electron diffraction pattern shows the hexagonal c-axis spot pattern of a single green rust crystal and the diffuse polycrystalline ring pattern of the nanoparticulate UO<sub>2</sub>.

**RIGHT** - High resolution TEM showing highly crystalline UO<sub>2</sub> nanoparticles. The particles are typically 2-9 nm in diameter, which is consistent with the 2-5 nm average particle size predicted by the EXAFS data modeling.

## Project Objectives

The research we are proposing addresses fundamental aspects of the effects of coupled biotic and abiotic processes on U speciation in subsurface environments where Fe redox cycling is significant. The long-term objective of this research is to evaluate whether reduction of U<sup>VI</sup> by biogenic GRs is a significant immobilization mechanism in subsurface environments. Our preliminary experiments have shown that biogenic GRs can reduce U<sup>VI</sup> to U<sup>IV</sup>; however, little is known about how biogeochemical conditions (such as pH, U concentration, carbonate concentration, and the presence of co-contaminants) and GR composition affect the rate and products of U<sup>VI</sup> reduction by GRs. It is also unclear which biogeochemical conditions favor formation of GR over other non-reactive Fe-bearing biomineralization products from the reduction of Fe<sup>III</sup> by DIRB. To address these issues, the following objectives are proposed:

- (1) Identify the geochemical conditions that favor the formation of biogenic GRs from the reduction of Fe<sup>III</sup> oxyhydroxides by DIRB (e.g., *Shewanella* and *Geobacter* species).
- (2) Characterize the chemical composition of biogenic GRs (e.g., Fe<sup>II</sup>:Fe<sup>III</sup> ratios and interlayer anions) and the effects of compositional variability on the rate and extent of U<sup>VI</sup> reduction.
- (3) Evaluate the effects of variations in geochemical conditions—particularly pH, U concentration, carbonate concentration, the presence of organic ligands, and the presence of reducible co-contaminants—both on the kinetics of U<sup>VI</sup> reduction by biogenic GR and on the composition of U-bearing mineral phases. Particular attention will be given to examining geochemical conditions relevant to conditions at DOE field sites.
- (4) Determine the potential for coupling the reduction of Fe<sup>III</sup> by DIRB to the reduction of U<sup>VI</sup> via biogenic Fe<sup>II</sup> species (including biogenic GRs).

The objectives outlined above will be achieved by testing the following hypotheses:

- (1) The formation of GRs by dissimilatory Fe<sup>III</sup> reduction is controlled by Fe<sup>III</sup> speciation, solution composition, and microbial physiology.
- (2) The chemical composition and structural properties of biogenic GRs are variable and depend on the conditions under which they were formed.
- (3) The rate of U<sup>VI</sup> reduction by biogenic GRs varies depending on their chemical composition and structure, particularly with respect to the Fe<sup>II</sup>/Fe<sup>III</sup> ratio and the nature of the interlayer anions.
- (4) The rate of U<sup>VI</sup> reduction by a given biogenic GR is affected by the solution composition (e.g., pH, uranium concentration, the concentration of carbonate and other ligands, and the presence of other potential oxidants). Moreover, the solution composition affects both the speciation of U<sup>VI</sup> and U<sup>IV</sup> and the stability of the GR.
- (5) The reduction of U<sup>VI</sup> to U<sup>IV</sup> can be coupled to dissimilatory Fe<sup>III</sup> reduction under conditions that promote the formation of biogenic GR and other reactive Fe<sup>II</sup> species.

The results of this research will increase our understanding of the coupling of biotic and abiotic processes with respect to the speciation of U in Fe<sup>III</sup>-reducing environments. This information has direct applications to understanding contaminant transport and the development of in situ bioremediation technologies for treatment of subsurface U contamination.

**Acknowledgement:** This work was supported by the U.S. Department of Energy, BER, NABIR Program, under Contract W-31-109-Eng-38. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38. MRCAT is supported by the Department of Energy under Contracts DE-FG01-904-ER45525 and the member institutions.